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博 士 学 位 论 文

福建沿海沉积物中邻苯二甲酸酯的地球化学

The Geochemistry of Phthalate Esters in Sediments of Fujian Coast, China

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摘 要

邻苯二甲酸酯（Phthalate esters, PAEs）是全球最普遍的污染物之一，具有急性毒性，致癌、致畸、致突变及生殖发育毒性。由于 PAEs 的疏水性，进入海洋环境中的 PAEs 容易吸附、转移和累积到沉积物中，沉积物是 PAEs 的一个重要归宿。沉积物中 PAEs 的地球化学研究，对于评价其污染水平和生态风险、理解其地球化学行为具有重要意义，也为污染控制和污染治理提供可靠的科学依据。

本文选择经济较为发达的福建沿海地区，以受人类活动影响较大的福建海湾为研究对象，分析测定了 13 个主要海湾表层沉积物及泉州湾柱状沉积物中 13 种 PAEs 的含量，研究了 PAEs 在福建沿海沉积物的水平和垂直分布特征、化学组成特征，探讨了影响沉积物中 PAEs 含量、分布和化学组成的因素，追溯了泉州湾区域 PAEs 的污染历史，得到以下结论：

（1）福建海湾表层沉积物中邻苯二甲酸酯的含量分布与化学组成

福建海湾表层沉积物中共检出 5 种 PAEs，分别为邻苯二甲酸二甲酯（DMP）、邻苯二甲酸二乙酯（DEP）、邻苯二甲酸二异丁酯（DiBP）、邻苯二甲酸二丁酯（DnBP）和邻苯二甲酸二（2-乙基己基）酯（DEHP）。各海湾 5 种 PAEs 总量（∑5PAEs）平均值由高到低依次为：厦门湾＞闽江口＞深沪湾＞福清湾＞泉州湾＞湄洲湾＞东山湾＞三沙湾＞沙埕港＞兴化湾＞旧镇湾＞罗源湾＞诏安湾。总体上，福建沿海表层沉积物的 PAEs 含量呈现南北海湾低、中部海湾及河口高的趋势，可能与各地区的经济发展水平和人口有关。此外，PAEs 的来源、沉积环境及沉积物性质都可能是影响沉积物中 PAEs 含量分布的重要因素。

DiBP、DnBP 和 DEHP 是福建沿海表层沉积物中主要的 PAEs 种类，3 种 PAEs 占∑5PAEs 的 92.10%~99.63%，平均百分含量为 96.25%。各海湾之间 PAEs 同系物间的化学组成不同，可能与周边地区 PAEs 的使用情况有关，在一定程度上反应了 PAEs 类化合物的消费结构。低分子量与高分子量 PAEs 的比值（LMW/HMW）表明：三沙湾、罗源湾、湄洲湾、深沪湾、东山湾、诏安湾、

兴化湾和旧镇湾等海湾沉积物中的 PAEs 主要来自化妆品和个人护理用品等产品中 PAEs 的释放；福清湾、泉州湾和厦门湾等区域沉积物中的 PAEs 以塑料制品中的增塑剂为主；沙埕港和闽江口沉积物中的 PAEs 则可能具有混合来源。

与国内外其他研究区域表层沉积物的 PAEs 含量相比，福建海湾表层沉积物的 PAEs 含量处于较低水平。根据 DnBP 和 DEHP 在沉积物中的生态风险阈值（ERL），福建海湾表层沉积物中的 DnBP、DEHP 和 DiBP 基本不存在生态风险。

（2）泉州湾表层沉积物中邻苯二甲酸酯的含量分布与化学组成

在 2009 年 3 月航次，泉州湾表层沉积物共检出 7 种 PAEs，分别为 DMP、DEP、DiBP、DnBP、DEHP、邻苯二甲酸二戊酯（DAP）和邻苯二甲酸双十一酯（DUP），7 种 PAEs 总量（∑7PAEs）的空间分布呈现晋江河口高于洛阳江河口，泉州湾南岸高于北岸，内湾高于外湾，潮间带随着离岸距离的增加∑7PAEs 逐渐降低的趋势。

泉州湾表层沉积物中 PAEs 以 DEHP、DiBP 和 DnBP 为主，3 种 PAE 组分之和占∑7PAEs 的 98.88%。主成分分析结果表明，泉州湾表层沉积物 PAEs 主要受两个因子控制，这两个主要因子解释 PAEs 方差的 70.40%，PAEs 的来源和理化性质可能是控制泉州湾表层沉积物中 PAEs 的主要因素。

与国内外其它研究区域 PAEs 含量相比，泉州湾表层沉积物中 PAEs 含量处于中等偏低水平。除个别站位的 DEHP 含量略高于 ERL，泉州湾表层沉积物中 DnBP 和 DEHP 基本不存在生态风险。

（3）泉州湾沉积物柱样中邻苯二甲酸酯的含量、垂直分布、化学组成及污染历史

泉州湾 3 个沉积物柱样（QZC1、QZC2 和 QZC3）共检出 6 种 PAEs，分别为 DMP、DEP、DiBP、DnBP、DEHP 和 DUP。各柱样 PAEs 的总体污染水平依次为 QZC3＞QZC1＞QZC2。总体上，PAEs 含量呈现上层高而底层低、随着深度增加而逐渐减小的垂直分布特征。

泉州湾柱样中的 PAEs 以 DEHP、DiBP 和 DnBP 为主，而 DMP、DEP 和

DUP 所占比例均较小。除 QZC1 柱样中 DMP 百分含量略高于 DUP 以外，各 PAEs 的百分含量依次为 DEHP＞DiBP＞DnBP＞DUP＞DMP＞DEP。各柱样 PAEs 分布模式的差异可能与与不同区域 PAEs 的消费结构有关。

^{210}Pb 定年法测得沉积物柱样 QZC1 的沉积速率为 1.3 cm/年，沉积年代为 1971~2011 年，历时 40 年。泉州湾沉积物中 PAEs 反映了泉州湾经济社会发展的四个阶段。

关键词：邻苯二甲酸酯；表层沉积物；沉积物柱样；福建海湾；泉州湾

Abstract

Phthalate esters (PAEs) are one group of pollutants most widely used worldwide, which have acute, reproductive and developmental toxicities and may cause carcinogenic, teratogenic and mutagenic effects. Due to their hydrophobic properties, PAEs in the marine environments are apt to be absorbed to particles and accumulated into sediments. Thus, the sediment is an important sink for PAEs. Geochemical studies on PAEs in sediments are important for evaluating the pollution degree and ecological risks, understanding their geochemical behaviors and providing scientific basis for the pollution control and environmental recovery.

This paper studied PAEs in the main bays of Fujian Province, southeast China, which were very typical since they were located in the developed Fujian coasts and were affected severely by anthropogenic activities. The concentrations of 13 PAEs in both surface sediments from 13 main bays of Fujian Province and 3 sediment cores from Quanzhou Bay were measured to study the horizontal and vertical distributions and chemical composition of PAEs in coastal sediments of Fujian. Factors affecting the concentration, distribution and chemical composition of PAEs in sediments were discussed and the pollution history of PAEs in the area of Quanzhou Bay was reconstructed. Main conclusions were:

(1) Concentration, distribution and chemical composition of PAEs in surface sediments from bays in Fujian

Five PAEs were detected in surface sediments from bays in Fujian, including dimethyl phthalate (DMP), diethyl phthalate (DEP), di-iso-butyl phthalate (DiBP), di-n-butyl phthalate (DnBP) and di 2-ethylhexyl phthalate (DEHP). The total concentration of 5 PAEs ($\sum$5PAEs) in these bays decreased as: Xiamen Bay > Minjiang Estuary > Shenhu Bay > Fuqing Bay > Quanzhou Bay > Meizhou Bay > Dongshan Bay > Sansha Bay > Shacheng Bay > Xinghua Bay > Jiuzhen Bay > Luoyuan Bay > Zhaoan Bay. Overall, the spatial distribution of the PAEs content in Fujian coastal surface sediments showed lower values in the southern and northern bays and higher values in the middle bays and estuaries,

which was probably associated with local economic development and population. The sources of PAEs, sedimentary environments and sediment properties were factors probably affecting the distribution of the PAEs content significantly.

DiBP, DnBP and DEHP were the main species of PAEs in surface sediments of Fujian coasts, which together accounted for 92.10%~99.63% of ∑5PAEs (mean: 96.25%). The chemical compositions of PAEs were different among bays in Fujian, which were probably dependent on the use of PAEs in the adjacent areas and to some extent reflected the consumption structure of PAEs. The ratio of low molecular weight to high molecular weight PAEs (LMW/HMW) suggested that PAEs in sediments originated mainly from cosmetics and personal care supplies in Sansha Bay, Luoyuan Bay, Meizhou Bay, Shenhu Bay, Dongshan Bay, Zhaoan Bay, Xinghua Bay and Jiuzhen Bay, from plasticizers in Fuqing Bay, Quanzhou Bay and Xiamen Bay, and from mixed sources in Shacheng Bay and Minjiang Estuary.

Compared with surface sediments from other areas in China and overseas, PAEs in surface sediments from bays in Fujian were low. Evaluating with the ecological risk limits (ERL) of DnBP and DEHP in sediments, DnBP, DEHP and DiBP in surface sediments from bays in Fujian almost did not have ecological risks.

(2) Concentration, distribution and chemical composition of PAEs in surface sediments from Quanzhou Bay

Seven PAEs were detected in surface sediments from Quanzhou Bay in March 2009, including DMP, DEP, DiBP, DnBP, DEHP, diamyl phthalate (DAP) and diundecyl phthalate (DUP). The total concentration of the 7 PAEs (∑7PAEs) was higher in Jinjiang Estuary than in Luoyangjiang Estuary, in the southern than in the northern bank and in the inner than in the outer bay. In addition, ∑7PAEs decreased with increasing distance to the land in the tidal zone.

PAEs in surface sediments from Quanzhou Bay were dominated by DEHP, DiBP and DnBP, which together accounted for 98.88% of ∑7PAEs. Principle component analysis showed that PAEs in surface sediments from Quanzhou Bay were dependent on two principle factors, which together accounted for 70.40% of the variance of PAEs. The source and physicochemical properties of PAEs were